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Juvenile Chemical Sediments and the Long Term Persistence of Water at the Surface of Mars

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Abstract

Chemical sediments and the aqueous alteration products of volcanic rocks clearly indicate the presence of water, at least episodically, at the martian surface. Compared to similar materials formed on the early Earth, however, martian deposits are juvenile, or diagenetically under-developed. Here we examine the role of water in facilitating various diagenetic reactions and evaluate the predicted effects of time and temperature for aqueous diagenesis on Mars. Using kinetic formulations based on terrestrial sedimentary geology, we quantify the integrated effects of time and temperature for a range of possible burial and thermal histories of precipitated minerals on Mars. From this, we estimate thresholds beyond which these precipitates should have been converted to the point of non-detection in the presence of water. Surface water has been shown to be at least episodically present in recent times. Nonetheless, the integrated duration of aqueous activity recorded over geologically long intervals by hydrated amorphous silica, smectite clays and Fe-sulfate minerals suggest that where these minerals occur water did not persist much beyond their initial deposition. This geochemical conclusion converges with geomorphologic studies that suggest water limitation during the late Noachian-Hesperian peak of valley formation and a still more limited footprint of water since that time. In addition to documenting the presence of water and its chemical properties, a complete assessment of

potentially habitable environments on Mars should address the timescales on which liquid water has persisted and the timing of aqueous episodes relative to major planetary events.

Keywords: Mars, water, life, silica, clay, sulfate

1. Introduction

Liquid water undoubtedly left its mineralogical mark on the ancient martian surface. Hydrated silicates (including clays), sulfates and (hydr)oxides occur in exposures of Noachian and Hesperian age (~4.2-2.0 Ga; Ga: billion years), reflecting both spatial and temporal variation in acidity, volatile content and redox state (Ehlmann et al., 2008a; Milliken et al., 2008; Mustard et al., 2008; Squyres et al., 2008). Questions of habitability, however, require that we go beyond simple presence/absence to investigate the chemistry and persistence of that water. Chemically benign conditions appear to surround carbonate and clay-bearing assemblages (Ehlmann et al., 2008a; Mustard et al., 2008), while saline minerals reflect a harsher chemical environment before liquid surface water was largely lost (Tosca et al., 2008).

Perhaps the most basic requirement for habitability is that liquid water persist long enough to mediate chemical evolution and sustain life once it arises. Here we discuss mineralogical evidence for a general lack of diagenetic maturation among chemical sediments on Mars. Juvenile precipitates – that is, precipitates that have undergone little diagenetic modification since formation -- identified from outcrop investigations and remote sensing appear to have formed during geologically brief episodes of liquid water on early Mars. The observation that these precipitates have persisted to the present further suggests that they have seen little liquid water *since* they formed. This conclusion is consistent with recent studies of

valley networks, drainage basins and impact crater degradation, which independently point to transient rather than persistent liquid water on early Mars and a declining geomorphic influence of water thereafter (Stepinski and Stepinski, 2005; Fassett and Head, 2008a; Fassett and Head, 2008b; Barnhart et al., 2009; Som et al., 2009).

2. Mineralogical evidence for juvenile chemical sediments

2.1 Opaline Silica

Silica commonly forms when water interacts with mafic rocks (McLennan, 2003). The relatively rapid dissolution of olivine, pyroxene and basaltic glass compared to other rock-forming silicates means that a significant amount of aqueous silica will be liberated during basaltic weathering. Consistent with this, opaline (hydrated, amorphous) silica has been identified in a number of locations on Mars. For example, geochemical mass balance and mini-TES analyses of evaporitic sedimentary rocks at Meridiani Planum show that the rocks contain significant amounts of hydrated silica, locally as high as ~20 wt.% (McLennan et al., 2005; Glotch et al., 2006). At Gusev Crater, opaline silica was identified in the Columbia Hills and interpreted as the product of intense aqueous activity, possibly related to hydrothermal processes (Squyres et al., 2008). Using orbital data, Milliken et al. (2008) identified opaline silica in the visible/near infrared (vis/NIR) using data from the MRO CRISM instrument. These latter deposits, many of which are associated with Fe-sulfates, are of Hesperian age and effectively expand the spatial and potentially temporal occurrence of opaline silica on ancient Mars. Recent data from the TES and THEMIS instruments further indicate large deposits of amorphous silica in western Hellas Basin (Bandfield, 2008). And more recently, a form of "hydrated silica" has been identified in Noachian terrains associated with detections of phyllosilicate minerals

74 (Mustard et al., 2008); these detections are, however, spectrally distinct from the opaline silica
75 deposits analyzed by Milliken et al. (2008). We refer to these phases as amorphous and
76 opaline/hydrated silica; as treated here, these include siliceous deposits in the form of coatings,
77 residual leachates, or phases precipitated from solution (which can contain a number of
78 compositional impurities).

79 On Earth, amorphous silica rarely persists through geologic time. Inevitably, diagenesis
80 results in the sequential production of opal-A, opal-CT, and, finally, microcrystalline quartz
81 (Williams et al., 1985). The critical material needed to direct this reaction series is liquid water.
82 At the molecular level, water drives the transformation of initially precipitated silica to less
83 soluble polymorphs by dissolution-reprecipitation (Williams and Crerar, 1985), a mechanism
84 supported by textural relationships among silica polymorphs, $^{18}O/^{16}O$ analyses, and both
85 thermodynamic and kinetic evidence (Williams and Crerar, 1985). This Ostwald Ripening
86 process indicates that initially amorphous silica will generally progress to cryptocrystalline or
87 microcrystalline quartz in the presence of liquid water. On Earth, amorphous silica is uncommon
88 in rocks more than several million years old (Maliva et al., 1989) because of (1) the rapid
89 reaction kinetics of silica diagenesis and (2) the accelerating effects of post-depositional burial
90 and heating characteristic of most sedimentary basins. Indeed, the oldest known amorphous silica
91 occurs in siliceous microfossils within deep sea muds and small nodules in New Zealand coals,
92 both of Cretaceous age; the common feature of these stratigraphic outliers is the encasement of
93 amorphous silica within sediments of unusually low permeability (Lawrence, 1993; Sykes and
94 Lindqvist, 1993; Ogawa and Kawata, 1998).

95 Why, then, should amorphous silica persist on Mars over billion year time scales? With
96 one exception, all known examples of free silica on Mars are hydrated and amorphous. The

97 exception is an orbital detection of quartzo-feldspathic materials thought to be a result of impact
98 differentiation processes, although this mechanism may not apply to the entire region (Bandfield,
99 2006). The TES instrument should detect quartz at a level above 5% (Bandfield, 2008), and,
100 although by definition quartz does not contain structural water, natural samples do (e.g., Aines et
101 al., 1984), and so detection (albeit difficult) could be possible with vis/NIR spectrometers such
102 as OMEGA and CRISM.

103 The preservation of opaline or amorphous silica for billions of years across a number of
104 localities at the ancient martian surface suggests that water could not have persisted at these sites
105 much beyond initial precipitation. Alternatively, the observed lack of diagenetic maturation
106 among silica-bearing sediments could be blamed on different styles of tectonism and
107 sedimentation between Earth and Mars, preventing martian sediments from experiencing Earth-
108 like post-depositional conditions. Siever (1983) presented a method by which the cumulative,
109 integrated effects of time and temperature on diagenesis can be quantified for sedimentary basins,
110 regardless of their burial and thermal histories. In the absence of plate tectonics for much of its
111 geologic history, most sedimentary basins on Mars formed from impacts (McLennan and
112 Grotzinger, 2008). In general then, the burial history of martian sediments is likely to reflect
113 cycles of burial and exhumation, with thermal history controlled principally by local geothermal
114 gradients. The geothermal gradient is in turn controlled by the thermal conductivity of bedrock
115 and sediment, as well as by heat flux, which, for Mars, is known to have reached a maximum
116 during the Noachian and subsequently declined (McGovern et al., 2002; Carr, 2007).

117 We begin by considering two endmember burial histories for Noachian and Hesperian
118 sediments: (1) early deep burial, with little subsequent exhumation until recently, and (2) the
119 maintenance of juvenile deposits near the martian surface for the majority of post-depositional

time. Figure 1 depicts these contrasting burial histories as a function of time and temperature. The first case assumes rapid burial to 2 km depth and thermal control by a deteriorating heat flux over time [specified by a function which fits heat flux as a function of age for various regions of the martian crust; (McGovern et al., 2002)], whereas the second case assumes little to no burial following deposition at or near the sediment/air interface. (In the second case, we assume near isothermal behavior for all of post depositional time.) Integrating under these curves gives the time-temperature integral (TTI) as a function of time, shown on Figure 2a, with a comparison to data for Paleozoic strata in the Illinois Basin (Siever, 1983; Moore, 2000). For the case of opal-CT conversion to quartz, we are interested in estimating a maximum threshold for conversion; that is, a single value representing any combination of time and temperature that will result in the complete (within detection levels) conversion of hydrated silica to quartz.

For Mars, maximum time would involve exposure to liquid water at 0^{o}C or less, with no heating. Where surface water is frozen, our current understanding of diagenetic mechanisms predicts that the lack of a liquid water phase would prevent diagenetic reactions from proceeding. Although the freezing point can be depressed by increasing salinity or acidity, the effects of high ion concentrations (and, by inference, low water activity, or a_{H2O}) on both the rate and mechanism of diagenetic reactions are largely unknown. High salinity and low a_{H2O} limit liquid water's availability as a solvent, and so reaction rates could either be increased as a result of water diffusion from the mineral phase to solution (in the case of silica diagenesis; Lasaga, 1998) or decreased by a lack of available solvent water. Ion concentration per se may also play a role, but like the effects of diffusion, this has not been quantified at high ionic strength. For these reasons, we have chosen to estimate the TTI threshold for 0^{o}C using: (1) observed siliceous

142 mineralogy in terrestrial sedimentary basins, and (2) kinetic formulations of the opal-CT to
143 quartz reaction.

144 Data from the Miocene Monterey Formation in California, which contains discrete zones
145 of opal-A, opal-CT and quartz, allow us to estimate the TTI threshold based on an empirical
146 burial history from initial amorphous silica deposition in a deep sea basin (Compton, 1991).
147 Using a known burial versus time curve (Compton, 1991), assuming initial deposition in 5^{o}C
148 seawater, and utilizing $^{18}O/^{16}O$ quartz formation temperatures ($\leq$ 62^{o}C) for the Monterey
149 Formation to set both lower and upper temperature limits for diagenesis (Matheney and Knauth,
150 1993), we arrive at a TTI threshold of about $0.4x10^{3}$ Ma·^{o}C. This value can be obtained either by
151 integrating an extended polynomial function fit to the time-temperature curve (constructed from
152 burial and temperature limits), or by simple integration by Riemann sums. For our martian case 2
153 (no deep burial, 0^{o}C), the equivalent time/temperature threshold would be reached after exposure
154 to water for about 400 Ma. A significant body of literature suggests that the kinetic rate law for
155 the opal-CT to quartz reaction holds at low temperature (<25^{o}C) because it involves dissolution
156 and reprecipitation reactions; the transition is known to occur at low temperature in a number of
157 terrestrial settings (Williams and Crerar, 1985; Williams et al., 1985; Botz and Bohrmann, 1991;
158 Matheney and Knauth, 1993).

159 As an alternative to geologically based estimates, we can estimate the conversion
160 thresholds using kinetic rate laws. For amorphous silica to quartz, conversion rates have been
161 estimated from experimental data collected at 300-500^{o}C (Ernst and Calvert, 1969), but
162 extrapolating a high temperature rate law to low temperature by means of the Arrhenius
163 relationship is not valid for the silica-water system. Both Lasaga (1998) and Dove (1995) stress
164 that the differences in activation energies, or temperature dependencies, derived for silica-water

reaction kinetics depend on the temperature range of investigation. Higher activation energies are associated with higher temperatures, where the faster process dominates the kinetics. Lasaga (1998) compared the activation energies for quartz dissolution derived by Dove and Crerar (1990) (19 kcal/mol at 200-300^{o}C) and Casey et al. (1990) (8.4 kcal/mol at 30-70^{o}C). The temperature at which the rates are equal and temperature dependencies "cross over" is 54^{o}C. This means that for temperatures of 54^{o}C and lower, there is a much lower temperature dependence on the quartz dissolution rate. Thus, extrapolation of the opal-CT to quartz reaction from very high to low temperature grossly overestimates the required time for conversion. Perhaps by coincidence, conversion times at ~70-25^{o}C are of the same order as natural observations, but the temperature dependence of the reaction is likely erroneous. A more realistic way to estimate opal-CT conversion would be to apply Casey et al. (1990)'s temperature dependence for low temperature silica reactions to the 25^{o}C opal conversion rate (based on high temperature kinetics) and then estimate the time required where liquid water at the martian surface was always at 0^{o}C. The estimate yields 330 Ma for total conversion of opal-CT to quartz at 0^{o}C, in reasonable agreement with TTI thresholds from the Monterey Formation. Although the kinetically-based estimate suffers from a lack of low temperature experimental data, it is likely to err in being too high – applying the low-temperature activation energy to high-temperature-based estimates above 25^{o}C would result in shorter conversion times. Continued extrapolation of this relationship to temperatures below 0^{o}C would extend even further beyond experimental and theoretical support. Aside from greater uncertainties associated with further temperature extrapolation, the extended presence of liquid water below 0^{o}C also requires knowledge of brine chemistry, introducing further uncertainty, as discussed above. Nonetheless, if we assume that diagenetic reaction rates below 0^{o}C decrease proportionally with temperature, then they must also decrease in proportion

188 to increasing salinity (and decreasing water activity, a_{H2O}). Of course, the larger question is
189 whether such cold saline fluids would have been habitable; that is, would the potential extension
190 of habitability conferred by freezing point depression be countered by ice formation and low
191 water activity? A recent examination of saline mineral parent waters on Mars suggests that this
192 possibility must be taken seriously (Tosca et al., 2008).

193 In summary, geological and kinetic data agree that, even at low temperatures, opal-CT
194 conversion takes place on geologically rapid timescales. Indeed, as noted above, amorphous
195 silica, whether opal-A or opal-CT, is rare in rocks older than a few million years (Maliva et al.,
196 1989). The paucity of amorphous silica older than ~145 Ma in terrestrial rocks independently
197 suggests that our estimates for TTI thresholds for opal-CT to quartz conversion are realistic
198 maxima (Fig. 2b).

199 For both martian post-depositional models, complete conversion to quartz occurs early;
200 the maximum threshold is surpassed in less than 100-400 Ma (Figure 2b). Simply put, when
201 water is present, precipitated opal-A or opal-CT that remains at or near a cold (0 ^{o}C) martian
202 surface converts completely to quartz in approximately 300-400 million years. Importantly,
203 whether water was present intermittently (e.g., with episodic absence by evaporation or freezing)
204 or continuously, our calculations are representative of *the total contact time* between a liquid
205 water phase and a given mineral after its formation. A number of factors might accelerate or
206 hinder the reaction progress of opal-CT conversion. Pressure, for example, will accelerate
207 conversion, as will any chemical process that removes $H_4SiO_4^0$ from the aqueous phase (e.g.,
208 complexation, adsorption, clay mineral formation) (Williams et al., 1985; Hinman, 1998; Huang,
209 2003). Alternatively, the reaction may be slowed by any "deactivation" of the reacting silica
210 surface (e.g., by Fe adsorption; Dove, 1995). Regardless of these second order influences,

however, liquid water is undoubtedly the catalyst for silica diagenesis. The persistence of amorphous silica on billion year time scales in Martian sediments suggests, parsimoniously, that these widespread deposits have seen very little water since deposition.

2.2 Smectite Clays

Clays comprise another important class of surface minerals on Mars. In general, Mg/Fe-smectites (e.g., nontronite, saponite) dominate martian phyllosilicate assemblages. In contrast, Al-rich clays, such as kaolinite, gibbsite and montmorillonite, are relatively rare (Mustard et al., 2008). A first-order comparison to clay mineral assemblages derived from terrestrial basalt indicates that the Mg/Fe-smectites found in numerous Noachian outcrops probably reflect a dry climate punctuated by episodes of aqueous activity. Although smectites are ubiquitous in most modern soils, exclusively smectitic soils on Earth rarely preserve in the geologic record.

The main reason why smectites don't preserve is that they transform diagenetically to more stable phyllosilicates (Weaver, 1989). The conversion of smectite into either illite (from dioctahedral smectite) or chlorite (from trioctahedral smectite) through burial diagenesis and/or metamorphism requires liquid water (Whitney, 1990; Altaner and Ylagan, 1997; Robinson et al., 2002). A recent examination of chloritization reaction pathways indicates that the fluid to rock ratio is key to reaction progress (Robinson et al., 2002).

At the molecular level, the hydration of cations to and from smectite, dissolution/reprecipitation of smectite/illite layers, and the introduction of excess OH^- (in chloritization) show that the reaction may not progress unless water is present (Whitney, 1990; Altaner and Ylagan, 1997; Robinson et al., 2002). Perhaps the most convincing evidence for water's role in catalyzing smectite conversion comes from experiments on the illitization of

234 smectite as a function of rock:water ratio (Whitney, 1990): the extent of illitization decreased
235 significantly with decreasing amounts of water. This inhibiting effect is most simply explained
236 by diffusion limitation. Decreasing water content leads to a greater fraction of unsaturated
237 porosity (i.e., wetted clay particles). As a result, the diffusion of ionic species to and from
238 smectite becomes increasingly controlled by surface diffusion, which is slow (Whitney, 1990;
239 Lasaga, 1998). Surface diffusion rates eventually become limited by increasing tortuosity and the
240 decreasing chemical gradient between solution and mineral, as solute concentrations build in the
241 fluid (Whitney, 1990; Lasaga, 1998). Diffusion across clay-bound water (i.e., at surfaces and
242 within interlayers), however, is only exacerbated by water's highly ordered nature, mainly from
243 electrostatic interactions (Sposito and Prost, 1982; Greathouse et al., 2000). In fact, for clays,
244 diffusion constants through surface and interlayer water have been estimated with molecular
245 dynamic simulations and are only a fraction of the bulk water value (Greathouse et al., 2000).

246 Smectite conversion is known to proceed under the effects of both temperature and time;
247 on Earth, discrete smectite (or illite/smectite with >5-10% smectitic layers) is rare in successions
248 older than ~600 Ma (Weaver, 1989). Returning to the time-temperature integral (TTI), it is
249 desirable to estimate TTI thresholds beyond which illitization would render smectite
250 undetectable on Mars. Again, estimates can be made using observed clay mineralogy in
251 terrestrial sedimentary basins and kinetic formulations of the smectite-illite reaction. For the
252 former, we focus our attention on terrestrial sedimentary basins where post-depositional thermal
253 history is well constrained. One of the best examples comes from studies of the Illinois Basin. In
254 particular, the Purington Shale (Pennsylvanian; ~310 Ma), buried to <1km and heated to no more
255 than 60^{o}C, preserves <10% smectitic layers in diagenetic illite/smectite (I/S) (Moore, 2000). The
256 thermal history of this formation is well constrained, yielding time-temperature integral curves

257 (Figure 2; Moore, 2000) that provide a robust estimate for the illite-to-smectite threshold on
258 Earth or Mars. Based on the threshold value provided by the Purington Shale (Figure 2b), we
259 estimate that at 0°C ~6 Ga are required to convert surface smectites to abundances below
260 detection limits.

261 Using reaction kinetics to estimate TTI thresholds for illitization is more difficult because
262 of the nature of the reaction mechanism. The temperature dependence of illitization has been
263 investigated experimentally and derived by fitting kinetic equations to illite/smectite mineralogy
264 in terrestrial sedimentary basins (Eberl and Hower, 1976; Bethke and Altaner, 1986; Velde and
265 Vasseur, 1992). As is the case for opal-CT conversion, high temperature experimental reaction
266 kinetics do not extrapolate well to low temperature. For illitization, however, they *under*estimate
267 the amount of time required for conversion, usually because smectite reacts more slowly as it
268 becomes progressively more illitic. A kinetic rate law introduced by Bethke and Altaner (1986)
269 takes this phenomenon into account and is consistent with illitization rates observed from a
270 number of basins. Adopting the same formulation and estimating the amount of time required to
271 convert smectite to >95% illite at 0°C, this approach yields a time estimate of ~9.2 Ga. It is
272 difficult to know whether the illitization reaction will proceed at such a low temperature.
273 Nevertheless, this equation estimates ~180 Ma for conversion to 80% illite at 35°C, which is in
274 good agreement with data suggesting that a maximum of 150 Ma was required to form 80% illite
275 under similar conditions from Lower Cambrian strata of the East European Platform (Kirsimae et
276 al., 1999).

277 We use TTI thresholds from both methods to establish maximum and minimum time
278 estimates for illitization on Mars, emphasizing that both estimates are consistent with
279 mineralogical and geological evidence on Earth and are equivalent to any combination of

280 temperature and time at the martian surface. The results show that burial or some other
281 modification of a near surface post-depositional environment is required to convert smectite to
282 illite (and/or chlorite) (Fig. 2b). It is well known that both illitization and chloritization occur at
283 low temperatures. Indeed, illite has been formed from smectite at room temperature in the
284 laboratory (Eberl et al., 1993) and at <35^{o}C in unheated sedimentary basins (Kirsimae et al.,
285 1999); chloritization has also been documented at <50^{o}C in natural settings (Walker, 1989; Eberl
286 et al., 1993). Kinetic data for the latter reaction are rare; however, chloritization involves many
287 of the same steps as illitization: the hydration and replacement of cations in octahedral and
288 interlayer positions and dissolution/reprecipitation steps (Robinson et al., 2002). Thus, the
289 estimate of illitization rates in Figure 2b is equally representative of the chloritization reaction,
290 showing that even minimal and possibly brief burial could be enough to cross the threshold
291 beyond which smectite declines to undetectable levels.

292 The TTI thresholds shown in Figure 2b represent an idealized case; a number of factors
293 could either accelerate or hinder reaction progress. For example, pore fluid chemistry (e.g., pH,
294 K^{+}, Al^{3+} and $H_4SiO_4^{0}$) plays a significant role, as does the composition of the initial smectite
295 (Altaner and Ylagan, 1997; Meunier, 2005). The former point deserves underscoring. The
296 observed lack of illitization could conceivably be blamed, at least in part, on lower available K
297 concentration in waters arising from a basaltic source. Chloritization (arguably the dominant
298 transition resulting from burial of trioctahedral smectites on Mars) does not require K, however;
299 and both reactions first require water.

300 The majority of phyllosilicates detected on Mars occur in rocks originally buried beneath
301 a substantial stratigraphic cover; in some cases, an overburden as thick as 4-5 km was present for
302 much of their post-depositional history (Mustard et al., 2008). Figure 3 shows the TTI curves for

303 smectite conversion as a function of initial burial depth. The burial and heat flux is the same
304 function as specified in Figure 1, but with the added constraint that as soon as a decay in global
305 heat flux brings shallow sediments back to surface temperature (i.e., 0^{o}C), the TTI curve
306 increases linearly with time. This analysis indicates that, at burial depths of 300m or greater (and
307 a continuous surface temperature of 0^{o}C), smectite deposited 3.5 Ga would have converted to
308 illite before the Hesperian ended. In addition, the *x*-axis on Figure 3 can be expanded to estimate
309 how long after initial formation smectites could be expected to convert as a function of burial
310 depth in the presence of water (Figure 4). The exact conversion times depend on rates of
311 sedimentation and burial, which, for the Noachian, may have been rapid, given denudation rates
312 inferred for this time (Hynek and Phillips, 2001). Importantly, local geothermal gradient will also
313 influence absolute conversion times. As discussed above, we can estimate the loss of primordial
314 crustal heat over time using estimates of crustal thickness from Mars Global Surveyor (e.g., the
315 shape of segment 3 shown in Fig. 1; McGovern et al., 2002), but detailed regional analyses of the
316 geothermal gradient must await a complementary understanding of the composition and
317 evolution of the martian crust.

318 Sedimentary deposits at Holden Crater, as well as the Eberswalde and Jezero fluvial
319 systems, all include smectite-dominated units that were buried to a minimum of a few hundred
320 meters following late Noachian/early Hesperian deposition (Ehlmann et al., 2008b; Grant et al.,
321 2008). In addition, Fe/Mg-smectites dominate stratigraphy at the bottom of the Noachian-
322 Hesperian Mawrth Vallis outflow channel, at a stratigraphic depth of approximately 600-700m
323 (Wray et al., 2008). At Nili Fossae, a smectite-rich basement unit is overlain by olivine-rich
324 deposits, which are in turn overlain by Syrtis Major lavas (Mangold et al., 2007). The
325 emplacement of these Hesperian volcanic units very likely exposed the underlying clay-rich units

326 to elevated temperatures, yet smectite remains the dominant clay. In comparison to Earth's
327 geologic record, where even the most benign post-depositional conditions have transformed
328 smectite older than ~600 Ma (Weaver, 1989), the persistence of smectite minerals on Mars is
329 striking.

330 Although the detection of more stable clay minerals (i.e., chlorite, illite, prehnite) has
331 been reported for some localities on Mars (Mustard et al., 2008), diagenesis/metamorphism is
332 only one of several potential mechanisms for their formation. In fact, these minerals may have
333 formed largely by impact-related hydrothermal processes, especially if their formation age is
334 contemporaneous with the large impact basins that covered ~43% of the martian surface during
335 late heavy bombardment (Frey, 2008). If minerals such as chlorite are in fact a major component
336 of martian clay mineralogy and we assume that they are exclusively the products of smectite
337 diagenesis/metamorphism, they must be reconciled with the dominance and persistence of
338 diagenetically immature smectites for billions of years at burial depths greater than a few
339 hundred meters, pointing to a conspicuous lack of diagenetic maturation. In other words, our
340 conclusions are based not on a lack of stable phases, but the persistence of their unstable
341 precursors. And because liquid water is known to catalyze the transformation of smectite through
342 cation hydrolysis and dissolution/reprecipitation, we once again conclude that a lack of post-
343 depositional water hindered diagenetic maturation.

344

345 *2.3 Fe-sulfate minerals*

346 At Meridiani Planum, late Noachian sandstones record the erosion of a salt-rich parent
347 lithology and subsequent, predominantly aeolian sedimentation, punctuated by intervals of
348 groundwater infiltration (Grotzinger et al., 2005; McLennan et al., 2005). The occurrence of Fe-

sulfate minerals throughout these sediments reflects a largely water-limited regime (Klingelhöfer et al., 2004; Poulet et al., 2008; Dickson and Giblin, 2009). In particular, the presence of abundant jarosite indicates a limited duration of groundwater percolation during diagenetic episodes (Elwood Madden et al., 2004). Thermodynamically, jarosite is metastable with respect to goethite and hematite; in water and over a range of pH, jarosite will transform to one or the other of these phases depending on chemistry, pH and temperature conditions within the sediment. Estimates of jarosite dissolution rates under various conditions indicate that, within errors typical of laboratory-derived dissolution rates, groundwater could not have persisted at Meridiani Planum for more than $\sim 10^1$ to 10^4 years, a timescale consistent with jarosite's disappearance from Rio Tinto terraces $\sim 10^4$ years old (Elwood Madden et al., 2004; Fernandez-Remolar et al., 2005; Smith et al., 2006). Similar arguments can be made for other Fe-sulfate phases based on their relative thermodynamic stabilities, but less is known about the dissolution behavior of these minerals.

At Meridiani Planum, the interaction of acidic water with a basaltic substrate would inevitably have led to an increase in pH through proton consumption and cation release. This would have displaced the equilibrium saturation of Fe-sulfate minerals (which are stable only at low pH) and initiated their decomposition. Thus, their occurrence points to short-lived aqueous episodes as a primary means of preservation. This line of evidence must also apply to other areas of the martian surface where acidic water was present, but did not persist long enough for increased pH (from basalt dissolution) to decompose the Fe-sulfates found in these localities. Many of the same strata that contain opaline silica are thought to contain ferricopiapite, an Fe-sulfate mineral which forms at pH on the order of 1 or less (Milliken et al., 2008). In addition, Mössbauer and APXS analyses show that Fe-sulfate rich soils at Gusev Crater contain abundant

372 rhomboclase and/or ferricopiapite (Morris et al., 2006). Schwertmannite, an iron oxy-
373 hydroxysulfate, rapidly decomposes to either jarosite or goethite over a range of pH and so its
374 preservation on the martian surface could also indicate a water-limited history. Schwertmannite
375 is one of several plausible candidates for the "nanophase ferric-oxide" signature in Mössbauer
376 spectra of Meridiani sedimentary rocks, but unequivocal mineral identification has not been
377 possible using the analytical tools on the MER rover Opportunity (Klingelhöfer et al., 2004).
378 The Rio Tinto system in southwest Spain provides a suitable analog for examining the
379 end products of an acidic system dominated by Fe sulfates. Rio Tinto is distinct from other areas
380 on Earth that are affected by acid mine drainage because the acid sulfate system is generated
381 naturally from pyrite oxidation and has been operating for 1-2 million years (Fernandez-Remolar
382 et al., 2005). Fernandez-Remolar et al. (2005) analyzed the ferruginous terraces deposited in
383 areas adjacent to the modern river channel and drainage system. The terraces reflect the
384 deposition and diagenesis of initially acid sulfate minerals – curiously, they record unusual
385 "popcorn" sedimentary textures that are thought to reflect the initial deposition of Fe-sulfates
386 such as copiapite, the dominant mineral cycling Fe and acidity between wet and dry seasons
387 (Fernandez-Remolar et al., 2005). The mineralogy of the terraces as a function of age shows that
388 Fe-sulfates are a transient phenomenon - over time and in response to diagenesis, they transform
389 to goethite (of varying degrees of crystallinity and magnetic ordering) and, finally, hematite. The
390 terraces become dominated by goethite and hematite in ~10,000 years, but more precise age
391 constraints on the terraces are lacking (Fernandez-Remolar et al., 2005). Although the precise
392 amount of time required to transform these phases to more stable Fe-oxide counterparts depends
393 on pH, the transformation is rapid, explaining the disappearance of such unstable minerals from
394 terrestrial systems more than several tens of thousands of years old. On Mars, the preservation

of Fe-sulfates for 3.5 billion years points to water limitation over the vast interval since deposition.

3. Discussion

3.1 Water availability during deposition

Without question, minerals exposed on the surface of Mars record the chemical action of water at their time of formation. But these minerals further allow the possibility that water availability was limited *during* sediment deposition, which we treat separately from the continuing influence of water *following* deposition (discussed below).

Studies of clay formation in basaltic rocks as a function of annually averaged precipitation point to a common characteristic of smectite development on Earth – a significant dry season. For example, Barshad (1966) focused on the mafic igneous rocks of the Sierra Nevada foothills, showing that smectites formed only in the driest climates. Gibbsite dominated the clay mineralogy in much wetter climates, with kaolinite representing a transition between the two. A similar study (Bates, 1960) on clays developed on Hawaiian basalt as a function of drainage and precipitation yielded the same results; smectite developed on the dry side of the islands while gibbsite formed in mountainous regions with heavy rainfall.

The development of Al-rich phyllosilicates from a basaltic lithology is dependent on a number of parameters, of which precipitation and drainage are among the most important. On Mars, Al-rich phyllosilicates are rare, and their spatially limited occurrence may actually be more consistent with alteration of discrete ash beds rather than abrupt changes in hydrology or climate. Pyroclastics tend to be composed mainly of glass, and this distinct difference in crystallinity would have drastically affected their dissolution behavior and the aqueous activity

418 of Al^{3+} (Tosca et al., 2004; Wolff-Boenisch et al., 2004). Experiments, modeling and field
419 studies all show that the alteration of glassy material results in more efficient production of Al-
420 rich phases, without the significant leaching and aqueous throughput normally required to
421 produce Al-rich weathering profiles (e.g., Mirabella et al., 2005). An analysis of the clay
422 mineralogy and stratigraphy at Mawrth Vallis, one of the few areas where Al-rich clays have
423 been identified on Mars, shows that Al-bearing phases are confined to specific strata that drape
424 local topography, consistent with airfall pyroclastic deposition (Wray et al., 2008).

425 While currently available evidence does not rule out persistent water over significant
426 areas at the time of clay formation, little that has been observed requires it. Moreover, as noted
427 above, estimates of water duration based on clay mineralogy must be evaluated in the context of
428 observed sulfate and silica mineralogy. We conclude that in many locations on the early martian
429 surface, water was present episodically, but not persistently. Whether this was generally true of
430 Noachian Mars will be clarified by continuing studies of chlorite and illites that will tell us
431 whether these are primary mineral phases formed during hydrothermal alteration or mature
432 precipitates produced by diagenetic conversion of smectites.

433 One last point: although the amount of clay minerals present in martian rocks is
434 substantial (e.g., Mustard et al., 2008), the *abundance* of water at a given time on the martian
435 surface should be treated separately from its *persistence*, which we have focused on above.

436

437 *3.2 Post-depositional water availability*

438 The juvenile nature of hydrated amorphous silica, smectite clays and Fe-sulfates
439 collectively reflects limited water availability during the long interval from initial deposition to
440 the present. As argued above, water (on molecular, microscopic, and regional scales) is the

441 catalyst that drives the diagenetic maturation of sediments that were themselves initially formed
442 in water. Because the effects of water with time is an inescapable driving force in the maturation
443 and diagenesis of chemical sediments, these hydrated precipitates record the additive effects of
444 interaction with liquid water, whether continuous or episodic, since the time of their deposition.

445 There is abundant evidence to suggest that liquid water was at least episodically available
446 up until the very recent geologic past and perhaps even the present (Renno et al., 2009; Schon et
447 al., 2009); relatively young gully features have been identified from orbit, with at least one
448 example allowing age estimates from crater counting at ~1.25 Ma. One hypothesis is that these
449 geomorphologic features are the product of snow melting following orbitally-forced climate
450 excursions and so are repeatedly episodic but individually short-lived (Schon et al., 2009).
451 Although no chemical precipitates have yet been tied to these occurrences (perhaps again
452 suggesting their limited interaction with surrounding sediment), the story told by much older
453 chemical sediments suggests that the integrated effect of transient liquid water at the surface of
454 Mars for the past several billion years has not been enough to drive their diagenetic maturation.
455
456 *3.3 Supporting evidence from geomorphology*
457 Chemical and geomorphologic evidence are converging on a view of early Mars in which
458 water was present, but intermittently so. Modeling studies exploring the nature of Noachian
459 valley networks agree that an arid climate is required to reproduce the observed drainage
460 characteristics – a wetter climate invariably produces features inconsistent with observed
461 topographic distributions and branching patterns and causes breaching of craters where water
462 could have ponded (Stepinski and Stepinski, 2005; Barnhart et al., 2009; Som et al., 2009). The
463 exact nature of the "arid" Noachian climate remains contentious, however. Stepinski and

464 Stepinski (2005) argue that the closest Earth analogs come from the Atacama Desert, a region
465 with negligible annually averaged precipitation. They also suggest that some features, such as
466 catastrophic outflow channels, could be the result of repeated short-duration episodes of aqueous
467 activity. Another study on the origin of valley networks in the Parana Basin requires an arid to
468 semiarid climate that lasted for a minimum of 10^3-10^4 years (Barnhart et al., 2009). The authors
469 stress the importance of episodic precipitation events that must have been punctuated by periods
470 of evaporation to produce the observed morphologies. Recent orbital analyses are consistent with
471 this conclusion. Chloride-bearing mineral assemblages are spread across a significant fraction of
472 Noachian terrains, with a number of deposits on crater floors (Osterloo et al., 2008). Although
473 there is currently little additional mineralogical evidence for Noachian evaporation (as clay
474 minerals constrain pH but not salinity), subsequent aqueous episodes may have redistributed
475 soluble salts from insoluble phyllosilicates until the global cessation of aqueous activity where
476 extensive saline deposits, the last vestige of liquid water on the ancient martian surface, were
477 permanently deposited. Nevertheless, application of a new crater counting technique to 30 valley
478 networks showed that valley networks are concentrated around 3.7Ga, with abrupt
479 disappearance after this time (Fassett and Head, 2008a).

480 Morphologic evidence shows that water was present on early Mars and was perhaps
481 abundant enough to leave signs of an integrated subsurface hydrology (Fassett and Head, 2008b).
482 Yet the conspicuous lack of diagenetic maturation among chemical sediments and the estimated
483 times required to create fluvial features on the martian surface suggests that total duration was
484 limited to a small fraction of geologic time and that aqueous activity in the Noachian was
485 episodic. As an exercise, we can assume that all valley networks identified by Fassett and Head
486 (2008a) are of different ages and that each lasted for 1 million years (probably both

487 exaggerations). The collective valley network record would then occupy about 1% of Mars
488 surface history over the last 4.2 billion years. We note, as well, that evidence for liquid water in
489 recent Mars history does not by itself require that water have been continuously present for the
490 past several billion years. A model published by Richardson and Mischna (2005), for example,
491 suggests that the probability of liquid water at the martian surface could be higher today than it
492 has been for much of the planet's history. In continuing studies it will be important to place the
493 timing and duration of aqueous activity more firmly in the context of planetary history.
494
495 **4. The duration of aqueous episodes on early Mars and implications for life**
496 Short-lived aqueous activity on the ancient martian surface could have influenced
497 habitability in significant ways. We do not know how long it takes to form life from abiotic
498 precursors; neither do we understand how long organisms can survive in the absence of water. If
499 surface water was available only intermittently and then vanished permanently, habitability of
500 martian surface waters may have been affected by the limited time to originate in or adapt to
501 chronically dry and/or potentially salty conditions before planetary water loss and significant
502 climate change (Tosca et al., 2008).
503 If habitable environments did exist on early Mars, they are separated from Meridiani
504 Planum and younger intervals by late heavy bombardment (Frey, 2008), the termination of the
505 magnetic dynamo (Lillis et al., 2008), and associated atmospheric loss (Greenwood et al., 2008;
506 Tian et al., 2009). Tian et al. (2009) have suggested that in its earliest history Mars could not
507 have accumulated a thick CO_2 atmosphere because high EUV would have allowed C to escape
508 from the top of the atmosphere at high rates. Thus the "wet" martian interval may have been
509 relatively short, beginning as EUV waned and ending with the loss of a magnetic shield. During

late bombardment, impacts recorded by giant craters would likely have sterilized the planetary surface (Sleep et al., 1989), with one of the last very large impacts, recorded by the ~1350 km Isidis Basin, forming at ~3.8-3.9 Ga (Frey, 2008). Thus, arguments about post-Noachian life on the martian surface require either that it originated *de novo* after late heavy bombardment in arid, acidic, and oxidizing conditions that would challenge prebiotic chemistry (Gabel and Ponnamperuma, 1967; Miller and Orgel, 1974; Tosca et al., 2008) or that it recolonized a forbidding post-Noachian surface from an unspecified subsurface refugium. Unfortunately, the sole example of life's origin does little to inform us of the necessary timescales for such a process, in large part because of the uncertain origin of self-replicating molecular systems (such as the so-called RNA world) which are thought to require a fortuitous combination of synthetic events (Orgel, 1998).

Life on Earth emerged early in the history of a watery planet. Much interest in the possibility that Mars also incubated living systems comes from the view that early in its history, our red neighbor was more similar to Earth than it is today. While late Noachian-early Hesperian Mars was certainly warmer and wetter than at present, evidence that it ever closely approximated the Earth remains to be discovered. More likely, the context for astrobiological consideration of Mars is an episodically wet planet that has been persistently dry for much of its history.

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533

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717

718 **Figure Captions:**

719

720 **Figure 1:** Conceptual time-temperature curves for two end-members of sediment burial on Mars.
721 The solid line represents the evolution of a sediment package upon: (1.) burial to 2 km depth
722 under an estimated Noachian heat flux (80 mW m^{-2}) and thermal conductivity of 2.5 W m^{-1} K^{-1},
723 (2.) constant burial depth at constant Noachian heat flux, and (3.) constant burial depth at a
724 decreasing heat flux. The dashed line represents deposition at the surface and isothermal post-
725 depositional behavior.

726

727 **Figure 2: (A)** Time-temperature integral values as a function of post-depositional time for the
728 two end-member burial scenarios depicted in Figure 1, and for the Upper Cambrian and
729 Pennsylvanian of the Illinois Basin, for reference. **(B)** Time-temperature integral curves from (A)
730 with a change in the *y*-axis scale to show thresholds for opal-CT to quartz conversion and
731 smectite conversion to illite. Threshold values are shown as horizontal lines, representing any
732 combination of temperature and time needed to convert hydrated silica and smectite to non-
733 detection. Both end-member burial scenarios cross the opal-CT detection threshold soon after
734 formation, whereas some burial or heating is required for smectite to completely convert to illite.

735

736 **Figure 3:** Time-temperature integral curves as a function of depth and post-depositional time.
737 Using the burial, geothermal and heat flux functions specified in Fig, 1, models show that burial
738 depths of ~300m and greater would convert smectite to non-detection.
739
740 **Figure 4:** Time temperature integral curves as a function of depth and post-depositional time
741 (Figure 3, with a change in the *x*-axis scale). According to this burial scenario, smectite buried to
742 1000m would be converted to non-detection in ~480 Ma.